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(54) PROTECTIVE LAYER CLOTHING MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a protective layer forming material, with which a protective layer uniformly and simply formed on the surface of an image produced by a heat transfer method under the condition that the resultant protective layer has enough hardness and flexibility developing neither crack n bend in combination.

SOLUTION: In this protective layer forming material, which is produced by peelably providing a layer containing an ultraviolet curable compound turning to s resin through curing on a support, the ultraviolet curable compound includes a urethane (meth) activate-based compound and a (meth)acrylate compound containing three or more functional groups.

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<u>CLAIMS</u>	<u>DETAILED DESCRIPTION</u>	<u>TECHNICAL FIELD</u>	<u>PRIOR ART</u>	<u>EFFECT OF THE INVENTION</u>	<u>TECHNICAL PROBLEM</u>	<u>MEANS</u>	<u>EXAMPLE</u>
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**CLAIMS**

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[Claim(s)]

[Claim 1] Protective-layer grant material to which an ultraviolet-rays hardenability compound is characterized by including an urethane (meta) acrylate system compound and the acrylate (meta) system compound of three or more organic functions in the protective-layer grant material which prepared the layer containing the ultraviolet-rays hardenability compound which hardens on a base material and may become a resin possible [ exfoliation ].

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the protective-layer grant method using the protective-layer grant material and this which can give in more detail endurance, such as abrasion resistance excellent in the protective-layer-ed grant material which has record of a picture etc., about protective-layer grant material, and can give the coloring nature which was further excellent in the picture etc., and glossiness.

[0002]

[Description of the Prior Art] In recent years, ID cards, such as licenses, an identification certificate, a membership card, and a card, come to spread, and use of a hot printing type ID card is performed. Since a full color picture can be easily the so-called sublimated type hot printing method especially using the coloring matter of heat translatability, it is a method effective in creation of an ID card. The ID card from which the picture was protected is indicated by JP, 6-286350, A. Since the ID card mentioned above was rubbed against the machine when the part recognized magnetical etc. was established and this part was made to recognize, although abrasion resistance was required, since pictures, such as a photograph of his face, a character, and a number, were inferior in endurance, especially abrasion resistance at the Records Department, the portion which is not recorded were damaged and they had the problem it becomes impossible to read information. Although there is also a method of making a picture side apply and harden a thermosetting resin paint and radiation-curing nature plastic paint as a method of solving such a trouble, the solvent in the paint invades a picture, and these methods have a possibility of carrying out strange tenebrescence, or cannot form a uniform application film easily, or a problem is in the shelf life of application liquid, or dust etc. adheres before and after an application and they have problems, such as soiling a screen. Moreover, although there is also a method to which a picture side is made to carry out hot printing (heat weld) of the protective layer by the hot printing method, the method of the hardness of a protective layer is insufficient, thickness is also thin again, and the protective layer which can satisfy endurance, especially abrasion resistance enough is not obtained. Then, after carrying out application dryness at the film sheet and carrying out heating sticking by pressure of the ultraviolet-rays hardenability compound beforehand with a binder, ultraviolet rays were irradiated and the method of exfoliating a film sheet and forming a protective layer in a picture side was developed after hardening an application layer. However, the protective layer made with the ultraviolet-rays hardenability compound could not obtain sufficient degree of hardness, but the blemish was sufficient for the front face just, and the injury might be received to the lower layer picture. Moreover, the protective layer created now although there was also an ultraviolet-rays hardenability compound which can obtain sufficient degree of hardness was weak, and when the transferred object was bent or it was made to deform, it had the problem that cracking cannot enter, or it was divided and the performance as a protective layer could not be satisfied.

[0003]

[Problem(s) to be Solved by the Invention] The purpose of this invention is forming a protective layer in the picture front face formed by the hot printing method simple uniformly, and is offering the protective-layer grant material which forms the protective layer having the flexibility which the formed protective layer has sufficient hardness, and produces neither a crack nor a crease.

[0004]

[Means for Solving the Problem] The above-mentioned purpose of this invention was attained by the protective-layer grant material to which an ultraviolet-rays hardenability compound is characterized by including an urethane (meta) acrylate system compound and the acrylate (meta) compound of three or more organic functions in the protective-layer grant material which prepared the layer containing the ultraviolet-rays hardenability compound which hardens on a base material and may become a resin possible [exfoliation]. The protective-layer grant material of this invention is put on protective-layer-ed grant material, after sticking by heat and the pressure, irradiates ultraviolet rays, and irradiates and forms the ultraviolet rays after an imprint by hardening or heat, and the pressure. The base material which had applied the protective layer exfoliates and is removed in front of irradiation of ultraviolet rays, or in the

back. Protective-layer-ed grant material is the material which wants to avoid the influence to the material which is easy to get damaged, the material which is easy to be worn, light, heat, a pressure, air (gases, such as oxygen etc.), and the front face from solvents (water, alcohol, etc.), and is material to carry out surface protection and surface reinforcement. For example, there are various record material, such as a photograph, a print, a telephone card, and an ID card, various plastics (a case, shelf, etc.), various miscellaneous-goods articles (shoes, a book, pencil, etc.), various cloth products (shoes, clothing, etc.), various metal goods (a signboard, griddle, etc.), various earthenware (a teacup, tile, etc.), etc. various record material, photographic recording material, printing material, sublimated type thermal-transfer-recording material, melting type thermal-transfer-recording material, thermal-transfer-recording material, ~~ink-jet material~~, sensible-heat material, platemaking printing material, etc. are mentioned. Especially, sublimated type thermal-transfer-recording material is desirable.

[0005]

[Embodiments of the Invention] The protective-layer grant material of this invention is explained below. The protective-layer grant material of this invention with the protective-layer-ed grant material which had information, such as a picture, recorded beforehand and/or a non-recorded protective-layer-ed grant material, and heat and/or a pressure. Pile up protective-layer-ed grant material and a hardenability protective-layer grant layer, and a hardenability protective-layer grant layer is hardened. By exfoliating a protective layer from the base material of protective-layer grant material, a protective layer is formed on a picture side, or a protective layer is formed by piling up protective-layer-ed grant material and hardenability protective-layer grant material with heat and/or a pressure, imprinting a protective layer from a base material, ~~and hardening by UV irradiation after ablation.~~

[0006] ~~The base material~~ conventionally known as a base material of the protective-layer grant material of this invention can be used. An example is shown below. First, a polyethylene terephthalate, polyethylenenaphthalate, a polyamide, A polycarbonate, a cellulose ester, an acetyl cellulose, fluorine polymer, A polyether, a polyacetal, a polyolefine, a polyimide, polyphenylene sulfide, Polypropylene, a polysulfone, cellophane, polyethylene, a polyvinylidene chloride, Polyvinyl alcohol, polyester, polystyrene, ethylene / vinyl acetate copolymer, Ethylene / vinyl alcohol copolymer, an ionomer, a polyvinyl acetal, Resin films, such as a polyvinyl chloride, a polyether sulfone, a polyether ether ketone, polyether imide, a polyacrylate, and a polymethylmethacrylate, various kinds of plastic film, ~~a sheet is used.~~

[0007] ~~The resin film of the above-mentioned base material may be used independently, and can also use the layered product by arbitrary combination.~~ Although it is desirable that it is generally the range of 2-360 micrometers as for the thickness of these base materials and it is still more desirable that it is the range which is 5-100 micrometers, since the optimum value on handling changes with quality of the materials of a base material, it is not restricted to the above-mentioned range. Moreover, you may give the under coat for raising detachability if needed. Among the above-mentioned base materials, what can bear processing temperature and the processing pressure force is desirable, and films, such as paper, a polyethylene-terephthalate film, polyester, a polycarbonate, and a polyamide, are desirable. Especially, especially the film of a polyethylene terephthalate and polyethylenenaphthalate is desirable.

[0008] The urethane (meta) acrylate compound of the radiation-curing nature resin which can be used for this invention makes a diol usually react to an isocyanate compound by the acrylate which has a urethane bond in a molecule (meta) and is compounded further (meta) by the acrylic ester and the ester exchange reaction. Various objects are marketed and an example is raised to below.

(a) urethane acrylate and urethane methacrylate -- for example The Toagosei chemical industry Co., Ltd. -- if it says with a tradename -- ARONIKKUSU M-1100, M-1200, and M-1300 -- if it says with the tradename of 1210, M-1250, M-126 M-1300, M-1310, and OSAKA ORGANIC CHEMICAL INDUSTRY, LTD. -- the screw coats 812, 823, and 832 -- new Nakamura chemistry Co., Ltd. -- if it says with a tradename -- NK ester U-4HA, U-108A, U-122A, and U-200 - AX, U-340AX, U-1084A, U-6HA, U-324A, and UA-100 grade is mentioned

[0009] ~~The object various with the acrylic ester (meta) of the alcohol of three or more organic functions in the ultraviolet-rays hardenability compound of three or more organic functions which can be used for this invention is marketed.~~ An example is raised to below.

(b) The ultraviolet-rays hardenability compound, for example, the pentaerythritol thoria chestnut rate, of three or more organic functions, Pentaerythritol trimethacrylate, pentaerythritol tetraacrylate, Pentaerythritol tetrapod methacrylate trimethylolpropane triacrylate, Trimethylolpropanetrimethacrylate, dipentaerythritol tetraacrylate, Dipentaerythritol tetrapod methacrylate, dipentaerythritol hexaacrylate, Dipentaerythritol hexamethacrylate, dipentaerythritol pentaacrylate, dipentaerythritol pentamethacrylate, a pentaerythritol polyacrylate, a dipentaerythritol polyacrylate, et are raised. Moreover, the ultraviolet-rays hardening compound of these three or more organic functions may be used combining two or more objects, may be mixture and illustrates a commercial thing below.

[0010] It will be NK ester if it says with the tradename of Toagosei Chemical industry with ARONIKKUSU M-309, M-305, M-309, M-310, M-315, M-320, M-325, M-330, M-400, and New Nakamura Chemistry tradename. TMPT, A TMPT, A-TMM -3, A-TMM-3L, A-TMMT, and A-9530 grade are mentioned.

[0011] A photoreaction initiator can be used into the radiation-curing nature constituent of this invention. As an example of a photopolymerization initiator, benzophenones, acetophenones, benzoin (a dichloro acetophenone, TORIKURORO acetophenone, etc.), thioxan tons, a Michler's ketone, a benzyl, benzoin alkyl ether, a benzyl dimethyl ketal, tetramethylthiuram monosulfide, an azo compound, etc. can be mentioned. these details -- "an ultraviolet-rays hardening system" (1989, comprehensive technical pin center, large) -- it is indicated by 63rd page - the 147th page e The content of such a polymerization initiator has per [ 0.5 ] ultraviolet-rays hardenability compound 100 weight section - 30 desirable weight sections, and its 2 - 20 weight section is especially desirable. Per ultraviolet-rays hardenability compound 100 weight section, the case of under the 0.5 weight section does not have a desirable cure r at the reasons of becoming extremely late, when ultraviolet rays are irradiated.

[0012] The ultraviolet-rays hardenability compound constituent of the protective-layer grant material of this invention may contain the binder. It may not dissolve, even if it dissolves with an ultraviolet-rays hardenability compound constituent as a binder, and the various resins which can generally form a film can be used. Preferably, protective-layer-ed grant material and an adhesive good resin are used. A binder and an ultraviolet-rays hardenability compound constituent are dissolved or distributed in a suitable solvent, and coating liquid is prepared and it is obtained by carrying out application dryness by the coverage which becomes 5-40-micrometer dryness thickness preferably about 2-100 micrometers, and forming a protective layer in one of said field of a base material, for example. As for such a binder resin, it is [ a metaphor ] desirable to use it at a rate of the about 20 to 600 weight section per ultraviolet-rays hardenability compound 100 weight section. It sets to this invention and a well-known solvent can use freely an above mentioned ultraviolet-rays hardenability compound constituent and an above-mentioned binder resin conventionally a solvent for dissolving or distributing.

[0013] Moreover, as the above-mentioned binder resin, all of a conventionally well-known binder resin can be used for such a purpose, and what has usually high thermal resistance is chosen. For example, a polyamide system resin, a polyester system resin, an epoxy system resin, a polyurethane system resin and the poly acrylic resin (for example, a polymethylmethacrylate --) Vinyl system resins including a polyacrylamide, polystyrene-2-acrylonitrile, and a polyvinyl pyrrolidone, A polyvinyl chloride system resin (a metaphor is a vinyl chloride vinyl acetate copolymer), A polycarbonate system resin, polystyrene, a polyphenylene oxide, a cellulose system resin (for example, a methyl cellulose, an ethyl cellulose, and a carboxymethyl cellulose --) Cellulose-acetate hydrogen phthalate, cellulose acetate propionate, a cellulose acetate butylate, a cellulose triacetate, and a polyvinyl alcohol system resin (for example, polyvinyl alcohol --) Partial saponification polyvinyl alcohol, such as a polyvinyl butyral, a petroleum system resin, a rosin derivative, coumarone-indene resin, a terpene system resin, a polyolefine system resin (for example, polyethylene, polypropylene), etc. are used. As a polyvinyl alcohol system resin, saponify polyvinyl acetate, consider as polyvinyl alcohol, a butyraldehyde is made to react to this, and it is compounded. As commercial elegance, things such as the DENKI KAGAKU KOGYO K.K. make and the Sekisui Chemical Co., Ltd. make, are known. As a polyvinyl butyral used for this invention, 70% of the weight or more, a with-an average degree of polymerization of 500 or more thing is desirable still more desirable, and polyvinyl-butyral contents are 1000 or more average degree of polymerization. as commercial goods -- the DENKA butyral 3000-1 by DENKI KAGAKU KOGYO K.K., 4000-2, 5000A and 6000C, and the Sekisui Chemical Co., Ltd. make -- S REKKU BL-1, BL-2, BL-3, BL-S, BX-L, BM-1, a BM- 2, BM-5, BM-S, BH-3, BX-1, and BX-7 are excellent

[0014] In addition to the above synthetic resin, these mixture or copolymers etc. can be used. A polyvinyl acetate-polyvinyl chloride copolymerization resin can be mentioned as a concrete copolymer. Moreover, acrylic resin and methacrylic resin are also mentioned. As acrylic resin, in a commercial tradename Mitsubishi Rayon Make -- diamon NARU SE-5437 and SE- 5102, SE-5377, SE-5649, SE-5466, SE-5482, and HR- 169, 124, HR-1127, HR-116, and H 113, HR-148, HR-131, HR-470, and HR-634 -- HR-606, HR-607, LR-1065, 574, 143, 396, 637, 162, 469 and 216, B 50, BR-52, BR-60, BR-64, BR-73, BR-75, BR-77, BR-79, BR-80, BR-83, BR-85, BR-87, BR-88, BR-90, BR-93, B 95, BR-100, BR-101, BR-102, BR-105, BR-106, BR-107, BR-108, BR-112, BR-113, BR-115, BR-116, BR-117, BR 118 grade can be mentioned.

[0015] As a protective-layer-ed grant material to which this invention is applied, record material is desirable, and what record material is for example, sublimated type thermal-transfer-recording material, it is desirable to use the binder with which the binder used for the television material of sublimated type record material, structure, and/or composition were alike as a binder which constitutes the protective-layer grant material of this invention. In a polyester system, a polyvinyl alcohol system, a polycarbonate system, the poly acrylic, etc., a polyester system, a polyvinyl alcohol system, a polycarbonate system, the poly acrylic, etc. have the desirable binder of the television material of sublimated type thermal-transfer-recording material, and, in the case of a radical polymerization, the binder of the protective-layer grant material of this invention also has an urethane acrylate system, acrylic, a specifically, desirable methacrylic system, etc. as an ultraviolet-rays hardenability compound of the protective-layer grant material of this invention.

[0016] The hardenability protective layer containing the radiation-curing nature compound prepared possible [ exfoliation of this invention ] may consist of layers more than two-layer. In this case, since the layer of the direction

near a base material turns into an outermost layer of film when a protective layer is formed, it is desirable to make the composition in which a film surface cannot get damaged easily, using a mat agent, a hardening agent, etc. in the high synthetic resin of a glass transformation point \*\*\*\*. Moreover, you may prepare stratum disjunctum in the layer of the direction near a base material. As stratum disjunctum, arbitrary material can be prepared possible [ exfoliation ] according to the composition of a hardenability protective layer. Or an adhesive property with material give a protective layer without using it is made the improving composition. or [ that the layer of the one distant from base material uses the lower synthetic resin of a glass transformation point, or makes necessary minimum the amount of the high-boiling point organic solvent and/or the mat agent used ] -- A hardenability protective layer may be protected on it, the exfoliating film may be prepared at the time of grant of a protective layer, and you may make it the composition which prevents failure of surface smeariness, adhesion with other matter, blocking with the material of oneself and others, etc. or [ moreover, / that the layer of the one distant from a base material uses the higher synthetic resin of a glass transformation point, or makes necessary minimum the amount of the high-boiling point organic and/or the mat agent used ] -- or it is desirable to consider as the composition which designed the optimum point which prevents failure of surface smeariness, adhesion with other matter, blocking with the material of oneself and others, etc. in the range which does not fall an adhesive property with material to give a protective layer without using it. Moreover in order to raise the hardness of a radiation-curing nature compound, and an adhesive property with material to give protective layer which faces, it is desirable to make it the composition which changed the content.

[0017] The hardenability protective layer containing the radiation-curing nature compound which this invention uses may be hardened by the hardening agent. When hardening the polymer of an organic-solvent system, the hardening agent indicated by JP,61-199997,A and 58-215398 each official report etc. can be used. Use of the hardening agent on an isocyanate system is [ as opposed to / polyester resin / especially ] desirable.

[0018] It can add into the radiation-curing nature compound constituent in this invention, combining suitably various kinds of additives, such as an antioxidant, an antistatic agent, a dispersant, a stabilizer, a pigment, lubricant, and a mat agent. Into a radiation-curing nature compound constituent, even if it checks hardening, you may use a tenebrescence inhibitor in the range which does not cause inconvenience practically. As a tenebrescence inhibitor, there is an antioxidant, an ultraviolet ray absorbent, or a metal complex of a certain kind, for example. As an antioxidant, there is a chroman system compound, a coumarane system compound, a phenol system compound (for example, hindered phenols), a hydroquinone derivative, a hindered amine derivative, and a SUPIRO indan system compound, for example. Moreover, a compound given in JP,61-159644,A is also effective.

[0019] There is a compound of a publication in JP,54-48535,A [ of benzotriazol system compounds (U.S. Pat. No. 3,533,794 specification etc.), 4-thiazolidone system compounds (U.S. Pat. No. 3,352,681 specification etc.), benzophenone system compounds (JP,56-2784,A etc.) and others ], 62-136641, and 61-88256 each official report etc. as an ultraviolet ray absorbent. Moreover, ultraviolet-absorption nature polymer given in JP,62-260152,A is also effective. As a metal complex, there is a compound indicated by a U.S. Pat. No. 4,241,155 specification, the 3-36th columns of a 4,245,018 specification, the 3-8th columns of a 4,254,195 specification, JP,62-174741,A, a 61-88256 official report (27) - (29) page, JP,1-75568,A, JP,63-199248,A each official report number, etc.

[0020] The example of a useful tenebrescence inhibitor is indicated by JP,62-215272,A (125) - (137) the page. Before protective layer is beforehand given from protective-layer grant material, protective-layer-ed grant material may be made to contain these tenebrescence inhibitors and ultraviolet-absorption material so that hardening may not be checked, and you may make it supply them to protective-layer-ed grant material from the exterior by the method of making it imprint from tenebrescence inhibitor supply material etc. among the radiation-curing nature compound constituent of protective-layer grant material. You may use the above-mentioned antioxidant, an ultraviolet ray absorbent, and a metal complex combining these comrades.

[0021] Surfactants various for the purpose, such as an application assistant, detachability improvement, slide nature improvement, antistatic, and development promotion, can be used for the composition layer in the radiation-curing nature compound constituent of protective-layer grant material. A nonionic surfactant, an anionic surfactant, an amphoteric surface active agent, and a cation nature surfactant can be used. These examples are indicated by JP,62-173463,A and 62-183457 each official report etc. Moreover, in case a release agent, a tenebrescence inhibitor, an ultraviolet ray absorbent, a fluorescent brightener, and other hydrophobic compounds are distributed in a water-soluble binder, it is desirable to use a surfactant as a distributed assistant. For this purpose, the surfactant of a 37-38-page publication of JP,59-157636,A is especially used for everything but the above-mentioned surfactant preferably.

[0022] A mat agent can be used for protective-layer grant material. As a mat agent, there is a compound JP,63-274944,A, such as a benzoguanamine-resin bead, a polycarbonate resin bead, and an AS resin bead, and given [ 63-274952 each ] in an official report other than the compound of a silicon dioxide, a polyolefine, or a polymethacrylate given in JP,61-88256,A (29) page.

[0023] You may include an organic fluoro compound in protective-layer grant material for the purpose, such as slide nature improvement, antistatic, and detachability improvement. As an example of representation of an organic fluoro



compound, hydrophobic fluorine compounds, such as solid-state-like fluorine compound resins, such as oil-like fluorine system compounds, such as a fluorochemical surfactant indicated by JP,57-9053,B octavus - 17 column, JP, 20944,A, and 62-135826 each official report etc. or a fluorine oil, or a tetrafluoroethylene resin, are mentioned.

[0024] You may make protective-layer grant material contain a release agent in the layer near the base material of a protective layer, and/or stratum disjunctum in this invention. As a release agent, each well-known release agent, such oil of surfactant:paraffin series, such as solids, such as an impalpable powder of a polyethylene wax, an amide wax, a silicon system resin and an impalpable powder of a fluorine system resin, or a wax-like matter:fluorine system, and phosphoric ester system, a silicone system, and a fluorine system, can use it conventionally. independent [ in addition to a non-denatured thing / in denaturation silicone oils, such as carboxy denaturation, amino denaturation, epoxy denaturation, polyether denaturation, and alkyl denaturation, ] as a silicone oil -- or two or more sorts can be used together and it can use As the example, the various denaturation silicone oils of a publication can be mentioned to the 6-18B page of the "denaturation silicone-oil" engineering data of the Shin-etsu Silicone issue. the amino denaturation silicone oil which has the cross linking agent of this binder, and the basis (for example, an isocyanate and the basis which can react) which can react when using into the binder of an organic-solvent system -- moreover, when carrying out emulsification distribution and using into a water-soluble binder, a carboxy denaturation silicone oil (for example product made from Shin-etsu Silicone : the tradename X-22 -3710) or an epoxy denaturation silicone oil (for example product made from Shin-etsu Silicone : tradename KF- 100 T) is effective

[0025] In this invention, protective-layer grant material may have an interlayer among each class, such as a base material, a protective layer, stratum disjunctum, and a glue line. According to the quality of the material to constitute an interlayer is a layer equipped with either of the diffusion prevention layers, such as a cushion layer and coloring matter, or these two functions or more, and serves also as the duty of adhesives depending on the case. The duty which prevents that heat translatability coloring matter diffuses especially diffusion prevention layers, such as coloring matter in a base material is achieved. Although organic-solvent fusibility is sufficient as a binder which constitutes this diffusion prevention layer even if water-soluble, a water-soluble binder is desirable and the binder of the above-mentioned protective-layer grant material or gelatin is desirable as the example.

[0026] You may make the protective layer which constitutes protective-layer grant material, a cushion layer, a diffusion prevention layer, and a glue line contain impalpable powders, such as a silica, clay, talc, the diatom earth, a calcium carbonate, a calcium sulfate, a barium sulfate, an aluminum silicate, permutite, a zinc oxide, RITOBON, titanium oxide, and an alumina, in this invention.

[0027] \*\* to the base material of the protective layer of the protective-layer grant material of this invention to apply the coating liquid for protective-layer formation can be applied using well-known methods, such as a double roll coating machine, a slit coating machine, an air knife coater, a wire bar coating machine, a slide hopper, spray coating, a blade coating machine, a doctor coating machine, a squeeze coating machine, a comma coating machine, a reverse roll coater, a transfer roll coater, an EKUSUTOROJON coating machine, a curtain coating machine, a die coating machine, a coat method with a gravure roll, the knockout

[0028] Heat and/or a pressure are used as a method of piling up the protective-layered grant material and protective-layer grant material of this invention. A general heat heating roller, a laminator, hot stamping, an electric heat board, thermal head, laser, etc. can be used for heat and/or a pressure.

[0029] Although the general example about the hardening method of the hardenability protective layer of this invention is given, it is not limited to below. When using electron beam irradiation, the field of a penetrating power and the hardening force to acceleration voltage is 100-1000kV, and it is desirable to make it the absorbed dose of one pass more preferably set to 0.5 - 20Mrad using a 100-300kV electron ray accelerator. The penetrating power of a low and electron ray has acceleration voltage or the amount of electron beam irradiation too lower than this range, hardening sufficient to the interior of a base material is not performed, and if too larger than this range, energy efficiency not only gets worse, but the influence which is not desirable will appear on [ , such as an on-the-strength fall of a base material and disassembly of a resin and an additive, ] quality. As an electron ray accelerator, any, such as an electro curtain system, a scanning type, and a double scanning type, are sufficient, for example. In addition, since hardening of electron ray hardening resin will be barred on the occasion of electron beam irradiation if an oxygen density is high, it is desirable to perform substitution by inert gas, such as nitrogen, helium, and a carbon dioxide, and to irradiate an oxygen density in the atmosphere preferably suppressed to 400 ppm or less 600 ppm or less.

[0030] In the case of UV irradiation, it is desirable to use the lamp of 80 or more W/cm. For example, there are a low pressure mercury lamp, a medium-voltage mercury-vapor lamp, a high pressure mercury vapor lamp, a metal halide lamp, etc., and there is also an ozone loess type with little ozone generating.

[0031] As a laser beam mentioned above, laser, such as ion gas laser like an argon or a krypton, copper, gold and a metal vapor laser like cadmium, a ruby and solid state laser like YAG, or semiconductor laser like the gallium arsenide emitted in a 750-870nm infrared region, can be used. However, in practice, semiconductor laser is effective in respect of small, a low cost, stability, reliability, endurance, and the ease of a modulation. As for protective-layer grant

material, it is desirable to contain the material which absorbs a laser beam strongly in the system using laser. If a laser beam is irradiated at hot printing coloring matter supply material, a light energy is transformed into heat energy, and this absorptivity material will transmit the heat to an immediately near radiation-curing nature compound, and will be heated to the temperature hardened. This absorptivity material accomplishes a layer to an adhesion side with the protective-layered grant material of a radiation-curing nature compound, and exists in it, and/or is mixed with a radiation-curing nature compound. It becomes irregular with the electrical signal showing the configuration of a protective-layer grant side, only the protective layer of the field which exists required is heated and hardened, and a laser beam forms a protective layer.

[0032]

[Example] Although an example is given to below and this invention is explained to it in more detail, unless the main point of invention is exceeded, it is not limited to the following examples.

(Example)

Production of protective-layer [-ed] grant material: Make into a base material the polyester film with 6 micrometers and a width of face of 50mm which prepared the heat-resistant slippage layer which becomes creation one side of R-R-4 hot-printing coloring matter supply material (1) from heat-curing acrylic resin, and set in the gravure ink for black prints the side which prepared the heat-resistant slippage layer of this base material in the field of an opposite side to the ink constituent for coloring matter supply stratification of the detection mark of 10mm length, and the following composition The coloring matter for sublimated type hot printing and a binder resin are variously changed, as shown Table 1, and the coverage after dryness is 1.2 g/m<sup>2</sup>. It applied to Junji Men by length of 100mm, and coloring matter supply material (1) was created so that it might become.

[0033]

hot printing -- ink constituent for ink constituent yellow layers for a coloring matter supply layer application Colorin matter (the following compound 1) 2.7 (g)

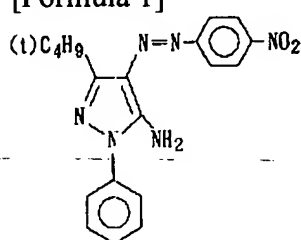
Coloring matter (the following compound 2) 0.3 (g)

Polyvinyl butyral (tradename by DENKA butyral 5000A DENKI KAGAKU KOGYO) 3 (g)

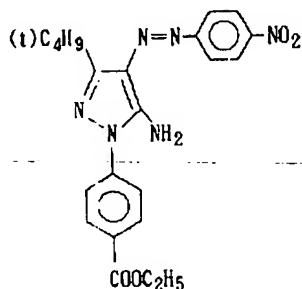
Silicone oil (tradename KFmade from Shin-etsu chemistry- 857) 0.05ml Toluene 50 ml Methyl ethyl ketone 50 ml P isocyanate (Takeda Chemical Industries tradename bamboo NETO 0.05ml D 110Ns)

[0034]

[Formula 1]



化合物 1



化合物 2

[0035]

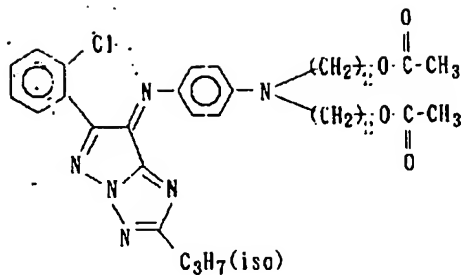
Ink constituent for Magenta layers Coloring matter (the following compound 3) 1.8 (g)

Coloring matter (the following compound 4) 1.2 (g)

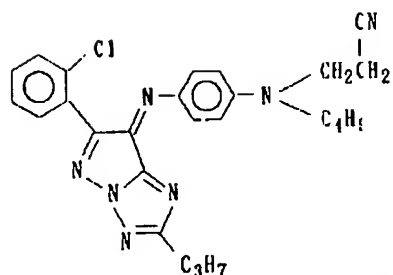
Polyvinyl butyral (DENKA butyral 5000A DENKI KAGAKU KOGYO make) 3 (g)

Silicone oil (tradename KFmade from Shin-etsu chemistry- 96) 0.05ml Toluene 50 ml Methyl ethyl ketone 50 ml P isocyanate (Takeda Chemical Industries bamboo NETOD 110Ns) 0.05ml. [0036]

[Formula 2]



化合物 3



化合物 4

[0037]

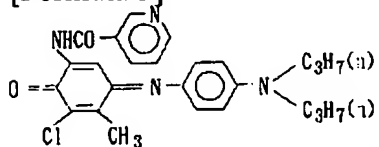
Ink constituent for cyano layers Coloring matter (the following compound 5) 1.8 (g)

Coloring matter (the following compound 6) 1.2 (g)

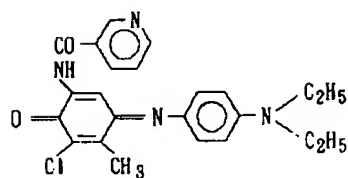
Polyvinyl butyral (DENKA butyral 5000A DENKI KAGAKU KOGYO make) 3 (g)

Silicone oil (KFmade from Shin-etsu chemistry- 96) 0.05ml Toluene 50 ml Methyl ethyl ketone 50 ml Poly isocyanate (Takeda Chemical Industries bamboo NETOD 110Ns) 0.05ml. [0038]

[Formula 3]



化合物 5



化合物 6

[0039] The coloring matter television layer application liquid constituent of the following composition on a laminated type vinyl chloride card with a creation thickness [ of the coloring matter television material R-1 ] of 760micro was applied so that the thickness after dryness might be set to 8 micrometers by the wire bar coating method, and the hot printing coloring matter television material R-1 was produced. Sample size was cut into 100mmx140mm.

[0040]

Constituent for a coloring matter television material application Polyester resin (TP220 : a tradename, the product made from a Japanese synthetic chemistry) 100g Silicone oil (KF-857 : a tradename, the product made from the Shin-etsu chemistry) 0.1g Poly isocyanate (KP90 : a tradename, Dainippon Ink make) 10g Methyl ethyl ketone 400ml Toluene 100ml. [0041] The constituent for a coloring matter television material application of the creation coloring matter television material R-1 of the coloring matter television material R-2 was changed to the following composition, and was produced like the coloring matter television material R-1.

Constituent for a coloring matter television material application Polyvinyl bromide CHIRU resin (S REKKU BLS : a tradename, Sekisui Chemical make) 100g Poly isocyanate (KP90 : a tradename, Dainippon Ink make) 10g Methyl et

ketone 400ml Toluene 100ml. [0042] The coloring matter television layer application liquid constituent same on a laminating type white polyethylene-terephthalate card with a creation thickness [ of the coloring matter television material R-3 ] of 760micro as the coloring matter television material R-1 was applied so that the thickness after dryn might be set to 8 micrometers by the wire bar coating method, and hot printing coloring matter television material (R was produced. Sample size was cut into 85mmx54mm.

[0043] The coloring matter television layer application liquid constituent same on a laminating type white polyethylene-terephthalate card with a creation thickness [ of the coloring matter television material R-4 ] of 760mic as the coloring matter television material R-2 was applied so that the thickness after dryness might be set to 8 micrometers by the wire bar coating method, and the hot printing coloring matter television material R-4 was produc Sample size was cut into 85mmx54mm. A television layer should touch a coloring matter dose respectively in the coloring matter supply material (1) and the coloring matter television material R-1 to R-4 which were obtained as mentioned above. it was made to pile each other up, and using the thermal head, on the conditions of a 0.3W [ /dot ] output and 12 dots/mm of dot densities, it came out two to 15 msec, pulse width was changed in stairway, the photograph-of-his-face image was printed, and the protective-layer-ed grant material R-1 to R-4 was formed from th base material side of hot printing coloring matter supply material

[0044] creation [ :P ] of protective-layer grant material it is \*\* of the following composition on a transparent polyethylene-terephthalate film with a -1 - a P-26 thickness of 100 micrometers -- the layer grant layer application liquid constituent was applied so that the thickness after dryness might be set to 22 micrometers by the wire bar coat method, and the protective-layer grant material P-1 to P-26 was produced Sample size was cut into 100mmx60mm. Constituent for a protective-layer grant layer application Binder resin (it indicates all over Table 1) . x g Radiation-curing nature compound (it indicates all over Table 1) y-1g Radiation-curing nature compound (it indicates all over Table 1) y-2g Reaction initiator (IRUGA cure 651) 4 g Methyl ethyl ketone 400ml Toluene 100ml. [0045]

[Table 1]

表 1

保護層 材料 No	バインダー樹脂	添加量 x (g)	紫外線硬化性化合物ウ レタン系アクリレート	添加量 y <sub>1</sub> (g)	紫外線硬化性化合物 多官能アクリレート	添加量 y <sub>2</sub> (g)	備 考
P-1	ポリエステル樹脂 TP220 (日本合成化学製)	60	ウレタンアクリレート U-6HA (新中村化学製)	24	ジベンチエジエイト-ルペンタヘキ シアクリレート A9530 (新中村化学製)	16	
P-2	"	60	"	20	"	20	
P-3	"	60	"	16	"	24	
P-4	"	60	"	12	"	28	
P-5	アクリル樹脂ダイナール BR87 (三菱レイヨン製)	60	"	16	"	24	
P-6	アクリル樹脂ダイナール BR87 アクリル樹脂 エスロン BLS (横水化学製)	48 12	"	24	"	16	
P-7	"	"	"	20	"	20	
P-8	"	"	"	16	"	24	
P-9	"	"	"	12	"	28	

[0046]

[Table 2]

表 1 (つづき)

保護層付与材料 No.	バインダー樹脂	添加量 x (g)	紫外線硬化性化合物ウレタン系アクリレート	添加量 y <sub>1</sub> (g)	紫外線硬化性化合物多官能アクリレート	添加量 y <sub>2</sub> (g)	備 考
P-10	アクリル樹脂/イソナー-B BR87 ブチラ-ルエスレック BLS (硬水化学製)	48 12	ウレタンアクリレート U-6HA (新中村化学製)	8	ジベンタエリスリトール-ヘキサアクリレート A9530 (新中村化学製)	32	
P-11	アクリル樹脂/イソナー-B BR87 ブチラ-ルエスレック BLS	56 14	ウレタンアクリレート U-4HA	15	トリメチロールプロパン トリメタアクリレート (新中村化学製)	15	
P-12	"	"		12	"	18	
P-13	"	"		15	ペンタエリスリトール リアアクリレート (新中村化学製)	15	
P-14	"	"		12	"	18	
P-15	"	48 12	ウレタンアクリレート U-324A	15	ペンタエリスリトール テトラアクリレート (新中村化学製)	15	
P-16	"	"	"	12	"	28	
P-17	"	"	"	12	トリメチロールプロパン トリメタアクリレート (新中村化学製)	28	
P-18	"	"	"	20	"	20	

[0047]

[Table 3]

表 1 (つづき)

保護層付与材料 No.	バインダー樹脂	添加量 x (g)	紫外線硬化性化合物ウレタン系アクリレート	添加量 y <sub>1</sub> (g)	紫外線硬化性化合物多官能アクリレート	添加量 y <sub>2</sub> (g)	備 考
P-19	アクリル樹脂/イソナー-B BR87 ブチラ-ルエスレック BLS	48 12	ウレタンアクリレート U-8HA	16	トリメチロールプロパン トリメタアクリレート ジベンタエリスリトール-ヘキサアクリレート	12 12	
P-20	"	"	"	16	ペンタエリスリトール テトラアクリレート ジベンタエリスリトール-ヘキサアクリレート	12 12	
P-21	"	"	"	16	"	6 18	
P-22	"	"	"	40		-	比較例
P-23	"	"	-	-	ジベンタエリスリトール ペンタ&ヘキサアクリレート A9530	40	比較例
P-24	"	"	-	-	トリメチロールプロパン リアアクリレート	40	比較例
P-25	ポリエステル樹脂 TP220	60	ウレタンアクリレート U-6HA	40	-	-	比較例
P-26	"	60	-	-	ジベンタエリスリトール ペンタ&ヘキサアクリレート A9530	40	比較例

[0048] The field and protective layer which give a protective layer for the protective-layer grant material P-1 to P-26 and the protective-layer-ed grant material R-1 to R-4 which were produced were piled up through 170-degree-C and 9kg pile/m<sup>2</sup>, and the 1mm [/second] laminator, it exfoliated and the base material of protective-layer grant material was irradiated for 5 seconds after that using the mercury-vapor lamp of 400W from 50mm distance. Moreover, after piling up the field and protective layer which give a protective layer for arbitrary protective-layer grant material and protective-layer-ed grant material among the above-mentioned combination through the same laminator and irradiated for 5 seconds after that using the same mercury-vapor lamp, the base material of protective-layer grant material was exfoliated. The material obtained at this time was shown in the following table 2.

[0049] The detachability of a protective layer was visually checked about the sample obtained at this time. Thing \*\* which O and a part peel or the adhesion side has floated what imprints completely and can exfoliate easily, and what has an inadequate imprint and the thing which can peel from an adhesion side easily or can be taken were made into The result depended on each material is shown in Table 2.

[0050] About the abrasion resistance of the protective layer of the obtained material, it is JIS. The amount of loads uniformly applied by 200g using the nose-of-cam radius of 0.1mm, and the sapphire needle of 60 degrees of vertical angles, and it examined using the surface-hardness-test machine on move speed 5mm/a second of conditions as indicated by K6718-1983, and it checked visually. That to which a blemish was not attached at all was made into thing x, to which O, thing [ of the grade in which the rubbed thin marks remain ] \*\*, and a blemish stick, and it splits finely or powder is attached. The result was shown in the following table 2.

[0051] The operation which returns a card for the obtained sample to +90 degrees to -90 degrees in parallel with a shorter side centering on the center section of the long side of a card is repeated 5 times. At this time, the bending section circumference on the front face of a protective layer was observed visually, and it was estimated as changele thing O and thing x which cracking and the crack have produced. A result is shown in Table 2.

[0052]

[Table 4]

表 2

No	保護層付与材料No	被保護層付与No	剝離性	耐摩擦性	耐折曲性	備 考
1	P-1	R-1	○	△	○	本発明
2	P-2	"	○	○~△	○	"
3	P-3	"	○	○	○	"
4	P-4	"	○	○	○	"
5	P-1	R-2	○	△	○	"
6	P-2	"	○	○~△	○	"
7	P-3	"	○	○	○	"
8	P-4	"	○	○	○	"
9	P-5	R-3	○	○	○	"
10	P-6	"	○	○	○	"
11	P-7	"	○	○	○	"
12	P-8	"	○	○	○	"
13	P-9	"	○	○	○	"
14	P-10	"	○	○	○	"
15	P-11	"	○	○	○	"
16	P-12	"	○	○	○	"
17	P-13	"	○	○	○	"
18	P-14	"	○	○	○	"
19	P-15	"	○	○	○	"
20	P-16	"	○	○	○	"
21	P-17	"	○	○	○	"
22	P-18	"	○	○	○	"
23	P-19	"	○	○	○	"
24	P-20	"	○	○	○	"
25	P-21	"	○	○	○	"
26	P-5	R-4	○	○	○	"

[0053]

[Table 5]

表 2 (つづき)

No.	保護層付与材料No.	被保護層付与No.	剝離性	耐摩擦性	耐折曲げ性	備 考
27	P-6	R-4	○	○	○	本発明
28	P-7	"	○	○	○	"
29	P-8	"	○	○	○	"
30	P-9	"	○	○	○	"
31	P-10	"	○	○	○	"
32	P-11	"	○	○	○	"
33	P-12	"	○	○	○	"
34	P-13	"	○	○	○	"
35	P-14	"	○	○	○	"
36	P-15	"	○	○	○	"
37	P-16	"	○	○	○	"
38	P-17	"	○	○	○	"
39	P-18	"	○	○	○	"
40	P-19	"	○	○	○	"
41	P-20	"	○	○	○	"
42	P-21	"	○	○	○	"
43	P-22	R-3	○	×	○	比較例
44	P-23	"	△	○	×	"
45	P-24	"	△	○	×	"
46	P-22	R-4	○	×	○	"
47	P-23	"	△	○	×	"
48	P-24	"	△	○	×	"
49	P-25	R-1	○	×	○	"
50	P-26	"	△	×	○	"
51	P-25	R-2	○	○	×	"
52	P-26	"	△	○	×	"

[0054] If the protective-layer grant material of this invention is used as shown in Table-2, it excels in productivity by simple operation, and the protective layer excellent in endurance, especially abrasion resistance can be further formed in protective-layer-ed grant material.

[0055]

[Effect of the Invention] If the protective-layer grant material of this invention is used, the ID card to which the protective layer could be given to the protective-layer-ed grant material which imprinted the picture of an ID card etc by easy operation, and the protective layer was given can give the property of excelling in abrasion resistance, crease proof nature and picture shelf life, and alteration-proof nature.

[Translation done.]